

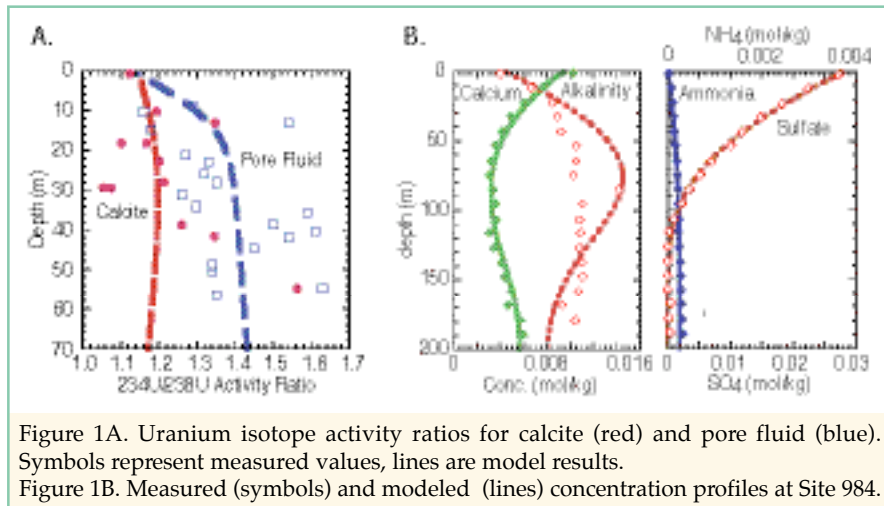
THE MINERAL DISSOLUTION RATE CONUNDRUM

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RESEARCH OBJECTIVES

The objective of this research is to determine whether mechanistic reactive transport modeling of uranium (U) isotopic profiles and major element chemistry (especially alkalinity and calcium) in marine sediments from the North Atlantic Ocean can be used to determine the origin of the apparent discrepancy between laboratory and field mineral dissolution rates.



APPROACH

Pore-water chemistry and $^{234}\text{U}/^{238}\text{U}$ activity ratios from fine-grained sediment cored by the Ocean Drilling Project (ODP) at Site 984 in the North Atlantic were used as constraints in modeling *in situ* rates of plagioclase dissolution with the multi-component reactive transport code Crunch. The reactive transport model includes a solid-solution formulation to enable the use of the $^{234}\text{U}/^{238}\text{U}$ activity ratios in the solid and fluid as a tracer of mineral dissolution.

A suite of reactions, including sulfate reduction and methane production, anaerobic methane oxidation, CaCO_3 precipitation, dissolution of plagioclase, and precipitation of secondary clay minerals, along with diffusive transport and fluid and solid burial, control the pore fluid chemistry in Site 984 sediments. The surface area of plagioclase in intimate contact with the pore fluid is estimated to be $3.2 \text{ m}^2/\text{g}$, based on both grain geometry and on the depletion of $^{234}\text{U}/^{238}\text{U}$ in the sediment via α -recoil loss. Various rate laws for plagioclase dissolution are considered in the modeling, including those based on (1) a linear transition state theory (TST) model, (2) a nonlinear dependence on the undersaturation of the pore water with respect to plagioclase, and (3) the effect of Al-inhibition.

RESULTS

The surface area of plagioclase in intimate contact with the pore fluid is estimated to be $3.2 \text{ m}^2/\text{g}$, based on both grain geometry and on the depletion of $^{234}\text{U}/^{238}\text{U}$ in the sediment via α -recoil loss. In the case of the linear TST model, the calculated dis-

solution rate for plagioclase corresponds to a rate constant that is about 104 to 105 times smaller than the laboratory-measured value. The major element and isotopic methods predict similar dissolution rate constants, if additional lowering of the pore water $^{234}\text{U}/^{238}\text{U}$ activity ratio is attributed to isotopic exchange via recrystallization of marine calcite, which makes up about 10–20% of the Site 984 sediment. Rate laws based on a non-linear dependence of the dissolution rate on the solution saturation state, or on inhibition of dissolution by dissolved aluminum, can only account for about one order of magnitude of the apparent discrepancy between laboratory and field rates.

The reactive transport simulations demonstrate that plagioclase dissolution rates depend strongly on the rate of authigenic clay precipitation, since clay precipitation controls both the saturation state of the fluid with respect to plagioclase and dissolved aluminum concentrations. Matching the range of aluminum pore-water concentrations found in deep marine sediments, it appears that slow clay precipitation and/or more soluble clay phases result in close-to-equilibrium conditions with respect to plagioclase, thus effectively removing two to three orders of magnitude from the overall mismatch between laboratory and field rate constants. The remaining two to three orders of magnitude must be attributed to the gradual loss of reactive sites on silicate surfaces with time, which is expected to be more pronounced under close to equilibrium conditions.

SIGNIFICANCE OF FINDINGS

The study indicates that the discrepancy between laboratory and field mineral dissolution rates is real in the case of plagioclase, and that this discrepancy can be attributed to the combination of a control on the saturation state of the plagioclase, exerted by clay precipitation, and the gradual loss of reactivity of the plagioclase surface itself over geologic time.

RELATED PUBLICATIONS

Maher, K., C.I. Steefel, and D. DePaolo, The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. *Geochimica et Cosmochimica Acta* (in press), 2005.

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